

The Importance of Intramolecular Conductivity in Three Dimensional Molecular Solids

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Recent years have seen tremendous progress towards understanding the relation between the molecular structure and function of organic field effect transistors. The metrics for organic field effect transistors, which are characterized by mobility and the on/off ratio, are known to be enhanced when the intermolecular interaction is strong and the intramolecular reorganization energy is low. While these requirements are adequate when describing organic field effect transistors with simple and planar aromatic molecular components, they are insufficient for complex building blocks, which have the potential to localize a carrier on the molecule. Here, we show that intramolecular conductivity can play a role in controlling device characteristics of organic field effect transistors made with macrocycle building blocks. We use two isomeric macrocyclic semiconductors that consist of perylene diimides linked with bithiophenes and find that the trans-linked macrocycle has a higher mobility than the cis-based device. Through a combination of single molecule junction conductance measurements of the components of the macrocycles, control experiments with acyclic counterparts to the macrocycles, and analyses of each of the materials using spectroscopy, electrochemistry, and density functional theory, we attribute the difference in electron mobility of the OFETs created with the two isomers to the difference in intramolecular conductivity of the two macrocycles.

Introduction

Understanding how molecular structure impacts mobility in organic field effect transistors (OFETs) has garnered much attention in recent years.^{1–6} Small, flat aromatic molecules, such as linear acenes, have been widely used as the active layer in organic semiconductors due to their relatively high carrier mobilities in both films and single crystal devices. The high carrier mobilities are attributed to strong intermolecular interaction amongst adjacent molecules and low intramolecular reorganization energy.^{7–9} While these two requirements govern charge transport for small, flat aromatic molecules, they are insufficient for complex, three dimensional molecules. In the latter, carriers can become localized, impeding transport. Examples of three dimensional molecular prototypes are fullerenes and fullerene derivatives,¹⁰ which are n-type materials used in OFETs,^{11–13} organic photovoltaics (OPVs),^{14–16} and organic photodetectors (OPDs).^{16,17} However, fullerenes are difficult to synthesize and functionalize, and their optical properties cannot be easily tuned. This prompts the search for alternatives that both absorb visible light and retain structural features, such as a three-dimensional shape.^{18–22}

Here, we study a sub-class of three dimensional, organic materials called conjugated macrocycles. Conjugated macrocycles possess

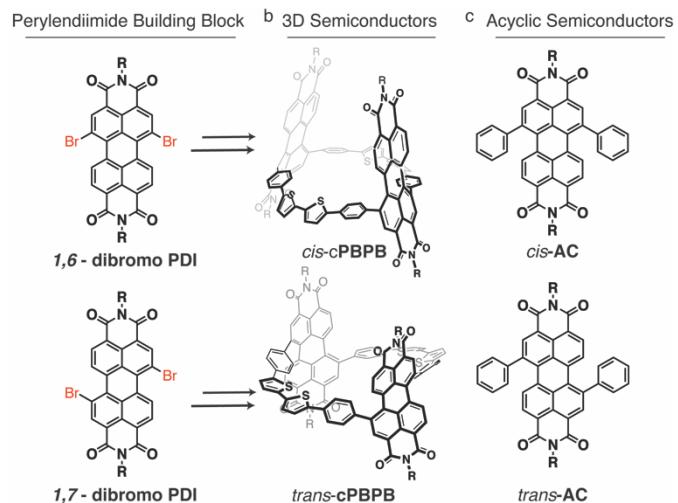


Figure 1 Structures of (a) 1,6 and 1,7-dibromo PDI, with the cis/trans orientation indicated in red; (b) *cis*-cPBPPB and *trans*-cPBPPB; and (c) structures of acyclic PDI derivatives. Cis- and trans-based semiconductors are derived from 1,6-dibromo PDI and 1,7-dibromo PDI, respectively. R = branched C₁₁H₂₃ side chains.

several structural and electronic advantages over acyclic molecules: 1) their contorted structure can facilitate intermolecular contact and charge transport;^{19,23} 2) they contain no end groups that can act as trap sites in linear molecules;^{24–27} 3) they often absorb more visible light than linear molecules;^{28,29} and 4) their intramolecular cavities can act as a host for electronic guests.^{30–35} We create OFETs with three dimensional molecular solids made from macrocyclic organic semiconductors illustrated in Figure 1, and describe the role of

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intramolecular conductivity on their performance. We find that intramolecular conductivity has an appreciable effect on the semiconductors' transport properties. While electronically active macrocycles have been used in organic devices such as transistors, photovoltaics and detectors in recent years,^{23,29,33,36-41} the impact of molecular structure on device performance is an ongoing field of research.⁴¹ Our macrocycles were designed to enhance intermolecular interactions through π - π coupling while allowing for synthetic flexibility to control their electronic properties.

Results

We utilize two types of perylenediimide (PDI) macrocycles that differ in their connectivity to the phenyl-bithiophene-phenyl linker: the PDI and linker are in a trans orientation for *trans*-**cPBPB** and cis orientation for *cis*-**cPBPB** (Figure 1b). *Trans*-**cPBPB** incorporates a 1,7-substituted PDI isomer into the synthesis while *cis*-**cPBPB** comprises a 1,6-substituted PDI isomer (Figure 1). We call these macrocycles **cPBPB**, where "c" = cyclic, P is diphenyl PDI, and B is bithiophene. We previously reported the synthesis of *trans*-**cPBPB**.⁴² We measure the device performance in OFETs, and show that

electrical mobilities are three times higher in the *trans*-based devices than in the *cis*-based devices. We study the materials on a single molecule level with macrocyclic components, use control experiments, computations, and spectroscopy to determine that the difference in electron mobility in OFETs made with the two macrocyclic isomers is due to the difference in intramolecular conductivity. This study demonstrates that intramolecular carrier pathways affect electron transport in three-dimensional molecular solids.

We first investigate the impact from the *cis*- or *trans*-linkage on the electrical properties of OFETs made using *trans*- and *cis*-**cPBPB** (Figure 2). Both *trans*-**cPBPB** and *cis*-**cPBPB** exhibit n-type characteristics and not p-type characteristics. To validate if the materials show any p-type characteristics, we set the source voltage at -80 V and swept the gate voltage to -80 V. From this measurement, we didn't observe any current in the negative gate region, which confirms the material doesn't show p-type characteristics. The devices show some leakage current due to the large difference between the gate voltage when we sweep from 80 V to -20 V and the source-drain current (80 V). The Supporting Information contains the

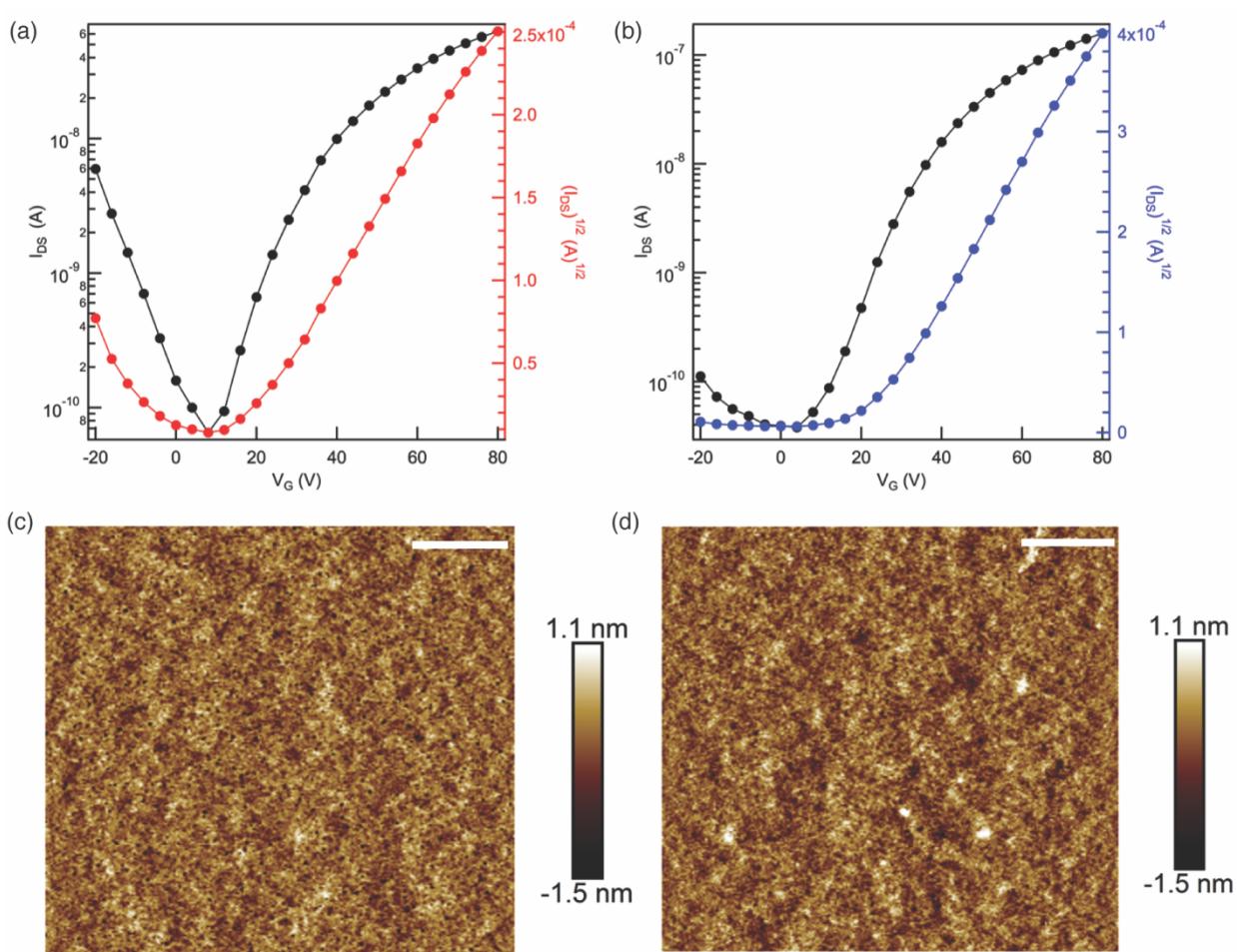


Figure 2 Electrical characteristics and morphology of the **cPBPB** OFETs. (a) transfer curve for *cis*-**cPBPB**; (b) transfer curve for *trans*-**cPBPB**. Device current (left axis, black) and square root of current (right axis, red or blue) measured as a function of gate voltage at a constant source-drain voltage of 80 V. The *trans*-**cPBPB** device has a higher current than the *cis*-**cPBPB** at a high and positive gate voltage, indicating a higher mobility for n-type carriers. (c) height image for *cis*-**cPBPB** and (d) *trans*-**cPBPB**. Both films are continuous and smooth and have a root mean square roughness of 0.35 and 0.37 nm for the *cis* and *trans*-based devices, respectively. The scale bar is 1.0 μ m.

output curves for the two macrocycles (Figure S1).

Figures 2a,b display the current versus applied gate voltages (transfer curves) for a trans and cis device. We collected the data for these transfer curves using a source-drain voltage of 80 V while sweeping the gate voltage from -20 V to 80 V. The mobility was calculated in the saturation regime^{3,43} using $I_{DS} = (W/2L)C_i\mu(V_G-V_T)^2$, where W and L are the width and length of the channel, C_i (11.5 nFcm⁻²), μ , V_G , and V_T correspond to the capacitance per unit area of the gate insulator, the field effect mobility, the gate voltage, and the threshold voltage, respectively. We find the mobility in *trans-cPBPB* is three times that in *cis-cPBPB* (1.3×10^{-3} cm²/V•s versus 0.4×10^{-3} cm²/V•s). We reproduce these mobility measurements across many samples. For example, we made ten devices with each isomer and found that the same values for the mobilities. Table 1 provides the averaged data for each macrocycle.

As morphology is known to have a profound effect on mobility, we first examined the film morphology using atomic force microscopy (AFM) to see if morphological differences could explain the difference in mobility.^{2,5,44,45} Both films were continuous and smooth, and had a room-mean-square roughness of 0.35 nm and 0.37 nm for *cis-cPBPB* and *trans-cPBPB*, respectively (Figures 2c,d). The powder/thin-film X-ray diffraction (PXRD) of both films too shows no signs of crystallinity (Figure S2). Taken together, the lack of difference (and the featurelessness of) in the PXRD and AFM data for the two isomers reveals that the difference in mobility cannot be attributed to morphological or crystallinity differences. Therefore, any differences in packing between the two isomers would need to be on an extremely short length scale.

We then used density functional theory (DFT) calculations to probe the differences in the molecular conformations and structures for *trans-cPBPB* and *cis-cPBPB*. Figure 3 contains the lowest energy structures for *cis-cPBPB* and *trans-cPBPB* determined from DFT using 6-31G/B3LYP level of computation. We see that the PDI units remain upright in *trans-cPBPB* while they bow inward toward the cavity in *cis-cPBPB*. The PDI-linker connection differs between the two isomers. The torsional angle is greater in the *cis* molecule relative to *trans-cPBPB*. This causes the PDI and linker to possess a relatively more orthogonal relationship, and decreases the electronic coupling in *cis-cPBPB* (Figures 3a,b). The colors of the macrocycles support *trans-cPBPB* is more conjugated: *cis-cPBPB* is purple by visual inspection, and *trans-cPBPB* is black.

We next consider the packing of these macrocycles with the crystal structure of *trans-cPBPB* (shown in Figure 3c and Supporting Information). We see that the macrocycles pack with the PDI face of one adjacent to that of another, though with opposite chirality.⁴⁶⁻⁴⁸ We were unable to obtain *cis-cPBPB*'s crystal structure, but anticipate a similar face-to-face packing, given the DFT-based structure presented here. The differences in the packing between the two isomers could result in an intermolecular effect on the conductivity that could also contribute to the difference in mobility, but we reiterate that the films are amorphous and featureless for each of the isomers.

In addition, its known that molecular strain and rigidity can influence charge transport in macrocyclic semiconductors with the more strained systems having lower intermolecular coupling

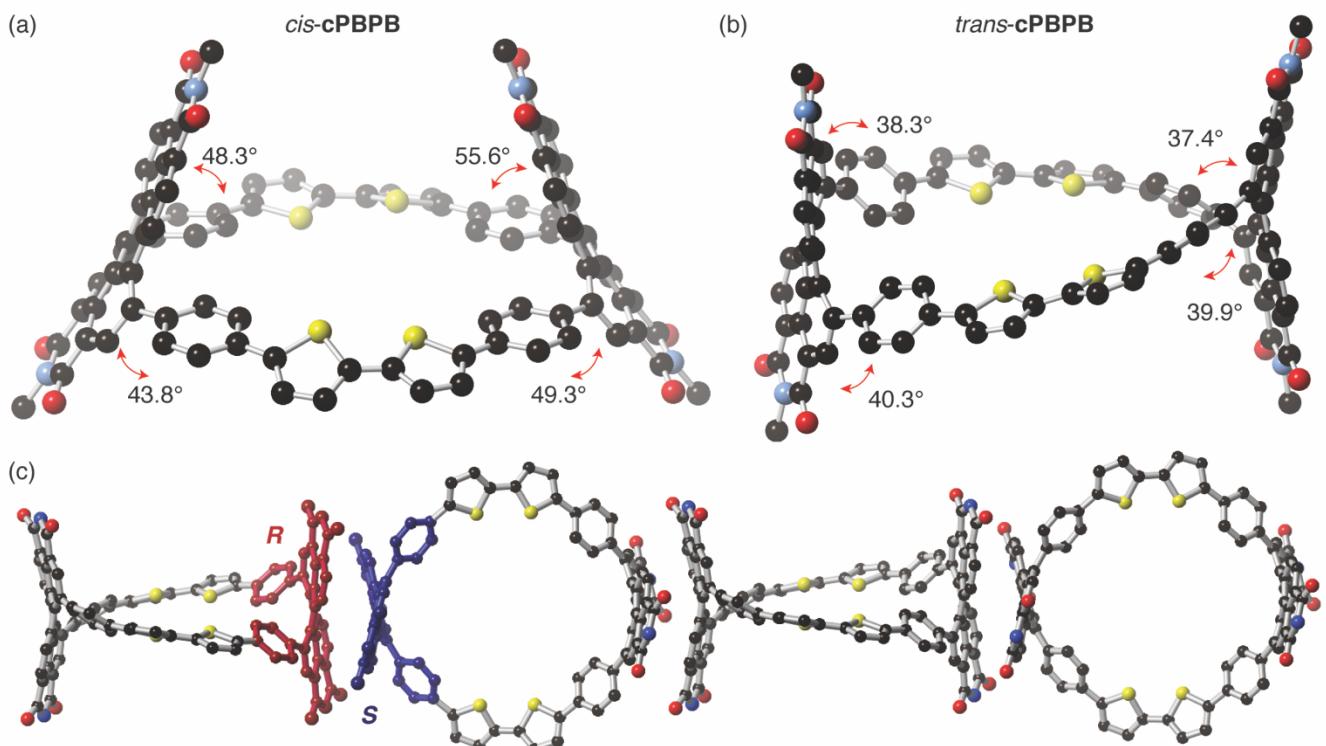


Figure 3 Molecular structures obtained with DFT using 6.31G*/B3LYP basis set. (a) *cis-cPBPB* and (b) *trans-cPBPB*. (c) SCXRD solid-state packing of *trans-cPBPB* as viewed down the a axis. Blue and red are the two enantiomers of the diphenyl PDI packing down the axis. Red = oxygen, blue = nitrogen, black = carbon, and yellow = sulfur. Hydrogens and side chains have been removed for clarity.



and hence lower intermolecular coupling and lower mobility.⁴¹ We calculate the enthalpy difference between the macrocycle and an acyclic analog (i.e., a homodesmotic calculation^{28,49–51}) to assess the strain energy in *trans*-**cPBPB** and *cis*-**cPBPB**. We found only a small (2 kcal/mol) difference in strain energy and therefore conclude that this does not explain the difference in mobility. The Supporting Information contains the details of the calculations used to assess the strain energy.

As these macrocyclic materials are n-type semiconductors, we wondered if a difference in reduction potentials would explain the difference in mobility. We used cyclic voltammetry (CV) to estimate the lowest unoccupied molecular orbital (LUMO) energies for both *trans*- and *cis*-**cPBPB** (Table 1, Figure S3). *Trans*-**cPBPB** and *cis*-**cPBPB** have similar reduction potentials, as estimated from the onset of the first reduction peak.⁵² We also examined the electronic structure using UV-Vis. The UV-Vis spectrum suggests *trans*-**cPBPB** is more conjugated. The lowest energy transition is at a lower energy in *trans*-**cPBPB** than in *cis*-**cPBPB**. Moreover, *trans*-**cPBPB** has a smaller optical gap than the *cis*-**cPBPB** macrocycle (Table 1, Figure S4). This likely reflects greater orbital overlap, given the smaller torsional angle between the linker and the PDI (Figures 3a,b).

Table 1: Comparison of *trans*-cPBPB** and *cis*-**cPBPB****

	Mobility μ $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$	LUMO level ^a (eV)	Optical gap ^b (eV)
<i>trans</i> - cPBPB	$(1.2 \pm 0.1) \times 10^{-3}$	-3.82	1.78
<i>cis</i> - cPBPB	$(0.4 \pm 0.1) \times 10^{-3}$	-3.79	1.85
<i>trans</i> - AC	$(1.5 \pm 0.3) \times 10^{-4}$	-3.74	2.10
<i>cis</i> - AC	$(1.9 \pm 0.3) \times 10^{-4}$	-3.74	2.10

CV, optical gap and FET performance for the two macrocycles and acyclic controls. ^a LUMO levels were estimated from onset of the first reduction peaks. ^b Optical band gaps were estimated from the onset of absorption.

We next evaluate the intramolecular conductivity by deconstructing the macrocycles into 1,6- and 1,7-diphenyl PDI monomers that possess two aurophilic amino groups on the aryl rings. We refer to these molecules as *trans*-**DAPP** and *cis*-**DAPP** (Figure 4a and Supporting Information III). While the cis and trans PDI isomers are well known,^{53–56} the difference in intramolecular conduction between the *cis* and *trans* isomers has not been reported until now. The two aurophilic amino groups on the aryl rings bind the Au electrodes in the STM-BJ setup^{57–60} to form Au-**DAPP**-Au- junctions (Fig. 4a). We found that *trans*-**DAPP** has a conductance nearly one order of magnitude higher than *cis*-**DAPP** at $\sim 8.6 \times 10^{-5} \text{ G}_0$ compared with $\sim 1.0 \times 10^{-5} \text{ G}_0$ (Figure 4b), where $\text{G}_0 = e^2/h$ is the conductance quantum. Figure S5 contains the

two-dimensional histograms for *cis*- and *trans*-**DAPP** and details for the experimental setup.

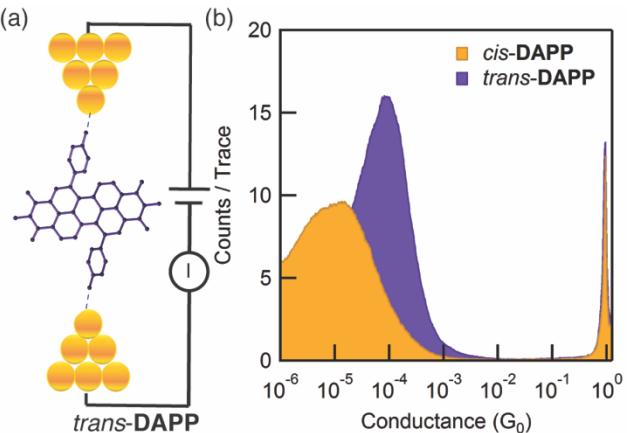


Figure 4 (a) Schematic of a single-molecule junction showing *trans*-**DAPP** in the break junction. The diphenyl PDI contains two aurophilic amino groups on the aryl rings to bind the gold electrodes in the junction; (b) Logarithm conductance histograms for *cis*-**DAPP** (yellow) and *trans*-**DAPP** (purple) measured with an applied bias of 450 mV in a 1,2,4-trichlorobenzene solution.

Because the STM-BJ studies determined that *trans*-substituted PDI molecular junctions are better conductors than *cis*-substituted PDI junctions, we hypothesized that the difference in the mobilities seen for *trans*- and *cis*-**cPBPB** based OFETs is due to the *trans*/*cis* substitution patterns. The experiments described next find that the substitution patterns in the acyclic subunits do not explain the differences in mobility between the two three-dimensional macrocyclic semiconductors, *cis*-**cPBPB** and *trans*-**cPBPB**.

We synthesized the acyclic relatives of *trans*- and *cis*-**cPBPB**, *cis*- and *trans*-**AC**, which comprise a diphenyl PDI substituted in a *cis* and *trans* orientation (Figure 1c). We made OFETs using *cis*- and *trans*-**AC**, and find that the two have similar averaged electron mobilities: $1.9 \times 10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$ and $1.5 \times 10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$ for *cis*-**AC** and *trans*-**AC**, respectively (see Table 1, Supplementary Table S1 and Figure S6 for details). We also studied the film morphology using AFM, and both films were smooth, with a root mean square roughness of 0.43 and 0.45 nm for *cis*- and *trans*-**AC**, respectively (Figure S7). Since *cis*-**AC** and *trans*-**AC** show similar mobilities in OFETs, the *cis* and *trans* substitution pattern alone is not the reason for the difference in the performance found in the macrocyclic systems.

Conclusions

Both *trans*-**cPBPB** and *trans*-**AC** possess a trans linkage, suggesting higher intramolecular conductivity than the *cis* analogues from the STM-BJ measurements. Yet OFET devices from either *trans*- or *cis*-**AC** show similar electron mobilities, while electron mobilities from *trans*-**cPBPB** or *cis*-**cPBPB**

macrocycles show marked differences in their mobilities. From this data, we conclude that the substitution pattern in the subunits is not responsible for the difference in charge transport in the acyclic controls, but influences charge transport for the relatively complex three dimensional semiconducting macrocycles. *Trans-cCPBPB* is more conjugated than *cis-cCPBPB*, as reflected in the UV-Vis data, suggesting that the intramolecular conductivity is higher in the *trans*-based macrocycle. Together, the acyclic control data, STM-BJ measurements, and spectroscopy demonstrate that intramolecular carrier pathways affect charge transport as the complexity of the molecule increases in molecular solids. For both isomers, the films are featureless, flat, and amorphous, implying that the morphology of the films and the crystal packing is not responsible for the difference in mobility. This study reveals the importance of not just intermolecular interactions and reorganization energy as conditions for electrical conduction in OFETs but also shows the importance of intramolecular conduction.

Conflicts of interest

There are no conflicts to declare.

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ASSOCIATED CONTENT

Supporting Information. Experimental procedures for the synthesis and characterization, UV-vis spectroscopy, cyclic voltammetry, STM-BJ setup and data, crystallographic data (CIF), OFET characterization, and computational details are contained in the Supporting Information. The Supporting Information is available free of charge on the ACS Publications website.

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Notes and references

‡ The current seen from the negative voltage is related to leakage current and does not represent an ambipolar device.

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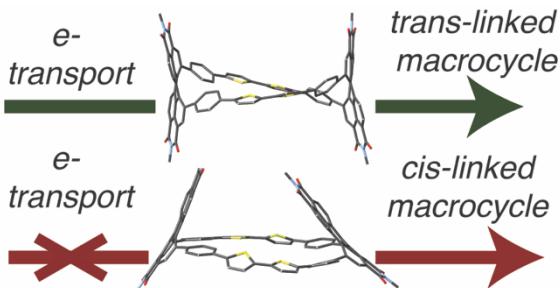
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TOC Entry



Trans-linked 3D-semiconductors have higher intramolecular conductivity.